

## CRYSTAL CHEMISTRY

# Crystal-Chemical Features of Diamonds Implanted with Helium Ions

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**Abstract**—Implantation of high-energy helium ions into crystals of natural colorless diamonds colors them bright yellow, brown, or black, depending on the implantation dose. The nature of the induced fantasy color and crystal-chemical features of the implanted diamonds have been investigated by IR spectroscopy and Raman spectroscopy. It is established that the radiation effect of helium ions on the diamond crystal structure results in the transformation of nitrogen-vacancy centers in its bulk with the formation of new *A*-type color centers, as well as the formation of carbon nanoclusters with the  $sp^2$  hybridization of bonds (which is typical of graphite) in black diamonds.

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## INTRODUCTION

Ion implantation, being one of the most efficient and fast methods of semiconductor doping with donor or acceptor impurities, has been applied for a long time and became popular in modern microelectronics for manufacturing large integrated circuits with a desired architecture on a semiconductor (generally silicon) wafer [1]. This method is based on the forced incorporation (implantation) of high-energy ions of various chemical elements into the surface layer of the irradiated solid substrate with any desired concentration, determined by the implantation dose. Being a highly productive method of modifying physicochemical properties of the surface layer of any irradiated material, ion implantation is also used in some other branches of the industry and natural science: metallurgy, medicine, chemistry, biology, etc. [1]. Moreover, the recent fundamental research in this field indicates that the technology of high-dose ion implantation (i.e., to a concentration that a priori exceeds the impurity solubility limit in the irradiated matrix) is promising for the synthesizing of nanocomposites with unique optical and magnetic properties [2, 3].

For the last 15 years, we have performed a series of studies focused on the influence of implantation with chromophore ions (the ions of iron transition group) on the optical properties of various minerals and their synthetic analogs [4–10]. A great experience in the forced (implantation-induced) change in the color of initially colorless minerals to different hues was accumulated by the examples of various silicate (beryl, adularia, topaz, etc.) and oxide (rutile, corundum, quartz, etc.) mineral matrices. The crystal-chemical

features of implantation-colored minerals made it possible to reveal the nature of induced color and determine the main mechanisms of localization of the implanted chromophore ions in the crystal structures of various minerals [5, 7, 8]. Note that similar studies on gemmological refinement of various raw minerals using ion implantation are also carried out abroad (in particular, works on implantation coloring of synthetic quartz [11], corundum [12, 13], and natural beryl [14] and topaz [15, 16] crystals, as well as the treatment of sapphire, ruby [17], and diamond [18]).

## EXPERIMENTAL

The objects of study were the faceted crystals of Ia-type natural diamond from Yakutsk deposits. Implantation of 40-keV singly charged  $\text{He}^+$  ions into diamonds was performed using an ILU-3 ion-beam accelerator at room temperature and ion-current density of 1.5–5.0  $\mu\text{A}/\text{cm}^2$  in vacuum (residual gas pressure of  $10^{-5}$  Torr). The implantation dose was varied from  $1.0 \times 10^{16}$  to  $7.5 \times 10^{16}$  ions/ $\text{cm}^2$ . In total, seven faceted diamonds were implanted with helium, and 21 cycles of ion implantation were performed in order to confirm reproducibility of the experiments aimed at desirable coloring of diamonds. At minimum implantation doses, diamonds became amber yellow, whereas at maximum doses they became black [19, 20]. An intermediate amount of the incorporated helium ions induced yellow-brown, brown, and dark-brown hues. A gemmological examination showed that the colors of implanted diamonds belong to highly decorative fantasy type. Investigations in a microscope in polarized